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TOWARDS MORE CONSISTENT ESTIMATES OF METHANE FLUXES BY THE EDDY COVARIANCE TECHNIQUE

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Academic dissertation

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Olli Pekka Peltola
University of Helsinki, 2016

Abstract

Methane (CH_4) is a strong greenhouse gas and its surface mixing ratio has increased by 150 % since the pre-industrial era. The aggregated atmospheric CH_4 budget is relatively well-constrained, however the contribution of different sources/sinks to the overall budget is not. The exchange of matter and energy between the atmosphere and different ecosystems can be studied with eddy covariance (EC) technique. Recently, instrumentation suitable for EC measurements of CH_4 fluxes have become available, however, measurement and data processing methodologies are yet to be standardised. By including instrument and software intercomparisons, this thesis is aimed to advance the harmonisation of EC CH_4 flux measurement and data processing methodologies. Data from two sites are utilized: Siikaneva fen in Southern Finland and Cabauw agricultural peatland in the Netherlands.

Improvement in CH_4 instrumentation was exemplified in this work by the decrease in the signal noise: the new CH_4 gas analysers showed approximately 10-times lower noise levels than the older models. Cumulative CH_4 emissions agreed within 7 % which suggests that there was no significant bias between the instruments. Another possible source of uncertainty is EC data processing. Two widely used EC data processing programs computed comparable CH_4 fluxes for different instrument and data processing combinations and thus the data processing routines were implemented similarly. The significance of careful EC data processing was demonstrated by the fact that occasionally the flux corrections contributed over 100 % of the measured signal. EC CH_4 fluxes showed high spatial variability in an agricultural peatland ecosystem, considerably higher than the other fluxes. The variability hinders the scalability of EC CH_4 fluxes to larger spatial scales and scaling is needed if the CH_4 balance of the whole landscape is evaluated. Therefore, the usability of tall flux tower to measure the landscape fluxes directly was also explored. While the results from this exercise were encouraging, the morning and evening transition periods proved to be difficult for the tall flux tower system.

This thesis sets a benchmark for the precision and accuracy of EC CH_4 data by evaluating instrumentation and data processing tools. Further, the thesis raises awareness of possible problems when upscaling short tower EC CH_4 measurements due to flux variability within the landscape. Finally, the findings can be used by researches in the future to evaluate the reliability of their EC CH_4 data and thus the thesis contributes to the harmonisation of EC CH_4 methodologies.

Keywords: eddy covariance, CH_4 flux, instrument intercomparison, data processing software, spatial variability, ICOS, wetland, agricultural peatland

Contents

List of publications

This thesis consists of an introductory review, followed by four research articles. In the introductory part, these papers are cited according to their roman numerals. **Papers I–III** are reprinted under the Creative Commons Attribution 3.0 License and the **Paper IV** under the Creative Commons BY-NC-ND license.

I **Peltola, O.**, Mammarella, I., Haapanala, S., Burba, G., and Vesala, T. (2013). Field intercomparison of four methane gas analyzers suitable for eddy covariance flux measurements, *Biogeosciences*, 10:3749–3765, doi:10.5194/bg-10-3749-2013

II **Peltola, O.**, Hensen, A., Helfter, C., Belelli Marchesini, L.,Bosveld, F.C., van den Bulk, W.C.M., Elbers, J.A., Haapanala, S., Holst, J., Laurila, T., Lindroth, A., Nemitz, E., Röckmann, T., Vermeulen, A.T. and Mammarella, I. (2014). Evaluating the performance of commonly used gas analysers for methane eddy covariance flux measurements: the InGOS inter-comparison field experiment, *Biogeosciences*, 11:3163–3186, doi:10.5194/bg-11-3163-2014

III Mammarella, I., **Peltola, O.**, Nordbo, A., Järvi, L. and Rannik, Ü. (2016). EddyUH: an advanced software package for eddy covariance flux calculation for a wide range of instrumentations and ecosystems, *Atmospheric Measurement Techniques Discussions*, doi:10.5194/amt-2015-323

IV **Peltola, O.**, Hensen, A., Belelli Marchesini, L., Helfter, C.,Bosveld, F.C., van den Bulk, W.C.M., Haapanala, S., van Huissteden, J., Laurila, T., Lindroth, A., Nemitz, E., Röckmann, T., Vermeulen, A.T. and Mammarella, I. (2015). Studying the spatial variability of methane flux with five eddy covariance towers of varying height, *Agricultural and Forest Meteorology*, 214–215:456–472, doi:10.1016/j.agrformet.2015.09.007

1 Introduction

In the absence of greenhouse effect the Earth's surface temperature would be -19 °C (e.g. Räisänen, 2008), on average, and thus life on Earth as we know it would be impossible. Luckily, the greenhouse gases (GHGs), of which the most abundant ones are water vapour (H_2O), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), create a "warm blanket" on top of the Earth's surface by limiting the outgoing longwave radiation and thus increasing the surface temperature. The atmospheric concentrations of the three latter GHGs have increased significantly since the pre-industrial era as a result of human activities and hence the energy balance of the atmosphere has changed. According to the IPCC 5th assessment report (Myhre et al., 2013) CO_2, CH_4 and N_2O are estimated to account for 64, 17 and 6 % of the present-day anthropogenic forcing, respectively. In other words, 87 % of the perturbation in Earth's energy balance is caused by the increase of these GHGs in the atmosphere. To inhibit the increase of atmospheric GHG concentrations and therefore in order to bring the Earth's climate back to the pre-industrial 'quasi-equilibrium', quantification of net exchanges of GHGs between the atmosphere and the Earth's surface at different spatial and temporal scales are needed.

During the last two decades the amount of micrometeorological flux measurements of these GHGs have notably increased. Micrometeorological methods are non-intrusive and non-destructive methods to measure ecosystem scale exchange rates of different compounds, such as the GHGs. The exchange is facilitated by turbulent mixing in the atmospheric boundary layer. The eddy covariance (EC) technique has emerged as the method of choice, since it is a direct way to estimate the ecosystem scale turbulent exchange and it can be used with relatively low maintenance needs (e.g. Aubinet et al., 2012). However, EC measurements do not directly relate to the surface flux, but several processing steps, in addition to a few assumptions, are needed before the fluxes can be inferred from the data (Mauder et al., 2007, 2008; Nordbo et al., 2012; Finnigan et al., 2003; Moncrieff et al., 1997; Webb et al., 1980). Traditionally researchers have been using custom-made codes for EC data processing, however this hampers the comparability of EC fluxes from different sites since differences between processing codes may cause apparent differences between sites. A few widely used software packages for EC data processing have been developed and cross-compared (Fratini and Mauder, 2014; Mauder et al., 2008).

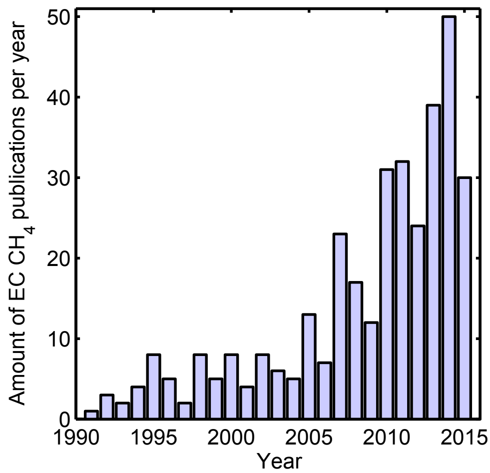

Figure 1: Amount of CH_4 eddy covariance publications listed in ISI Web Of Science (Data acquired 21.10.2015).

Several international networks utilize micrometeorological flux towers for direct measurement of CO_2, water vapour, sensible heat and momentum fluxes, whereas similar multi-year measurements of CH_4 have been less common. However, during the last decade EC CH_4 studies have become more ordinary (Fig. 1), and this increase is fuelled by the rapid development of instruments which are suitable for EC CH_4 flux measurements. In order to ensure that the instruments measure comparable fluxes, so far only a few field intercomparison studies have been carried out (Iwata et al., 2014; Detto et al., 2011).

One of the main difficulties in estimating ecosystem CH_4 budget is that the CH_4 fluxes tend to show significant spatial and temporal variability within an ecosystem (Waddington and Roulet, 1996; Riutta et al., 2007; Hendriks et al., 2010; Schrier-Uijl et al., 2010a,b; Teh et al., 2011) and thus it is difficult to assess how representative of the wider geographic area the flux measurements are. In order to translate the measured CH_4 emissions into continental and global CH_4 budgets, the measurements need to be scaled up, i.e. make an assumption that the obtained measurements and derived ecological responses describe a larger area than what was *de facto* measured. Upscaled CH_4 emissions have considerable uncertainties and the agreement with other large scale flux estimation methods (top-down inversion modelling estimates) is inadequate at continental (Schulze et al., 2009) and global (Kirschke et al., 2013) scales, which is calling for a methodological study.

The general aim of this thesis is to quantify the random and systematic uncertainties related to the ecosystem scale CH_4 emissions and in the case of systematic uncertainties, develop methods to minimize them. Thus the emphasis of this study is not on the CH_4 emissions themselves, but rather on the measurement method evaluation and development. Such studies help scientists who are applying the EC method to evaluate the reliability of their CH_4 flux measurements. The contents of this thesis are illustrated in Fig. 2. More **detailed aims** of this thesis are:

1) to quantify the random and systematic variation between EC CH_4 flux instrumentation (**Papers I,II**);

2) to assess the impact of different EC data processing routines on the CH_4 fluxes and to cross-compare the implementation of these routines between two data processing software products (**Papers I,II,III**);

3) to determine the spatial representativeness of short tower EC CH_4 fluxes in an agricultural peatland landscape (**Paper IV**);

4) to evaluate the applicability of a tall flux tower EC system in measuring landscape scale CH_4 emissions (**Paper IV**).

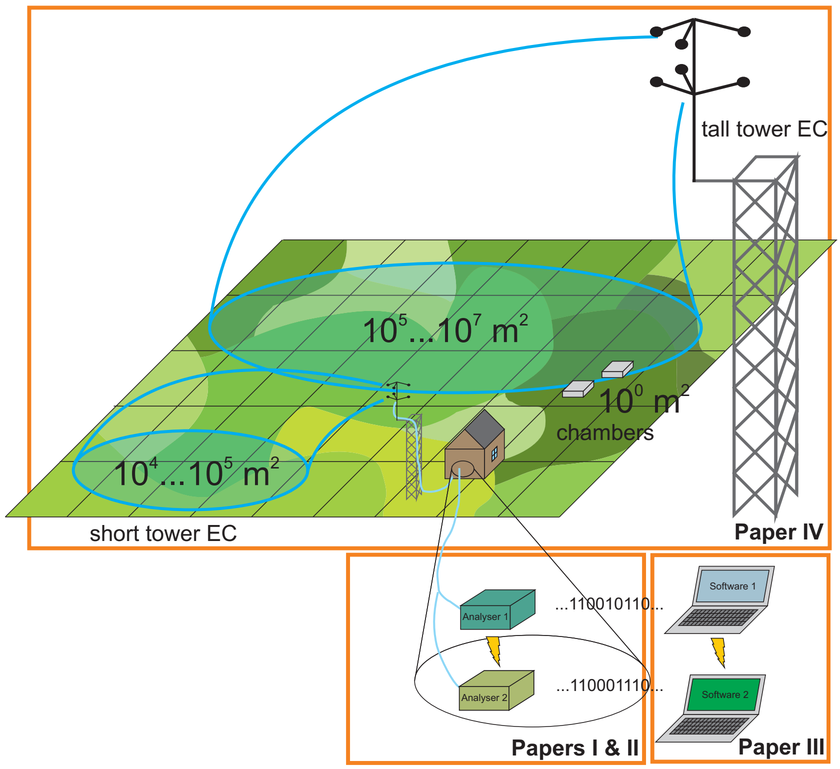

Figure 2: Schematic figure of the contents of the PhD thesis. Variations in the green color depict the spatial variability of the surface CH_4 flux and the blue circles show sizes of flux measurement source areas. **Papers I** and **II** deal with CH_4 instrument intercomparisons, **Paper III** presents comparison of two EC data processing software programs, and the **Paper IV** compares tall flux tower and short tower eddy covariance CH_4 measurements, i.e. flux measurements at different spatial scales.

2 Background

2.1 The atmospheric boundary layer

Atmospheric boundary layer (ABL) is the lowest part of the atmosphere and it is in constant interaction with the underlying surface (e.g. Stull, 1988). The flow field and the air composition within the ABL are modified by the surface interactions within an

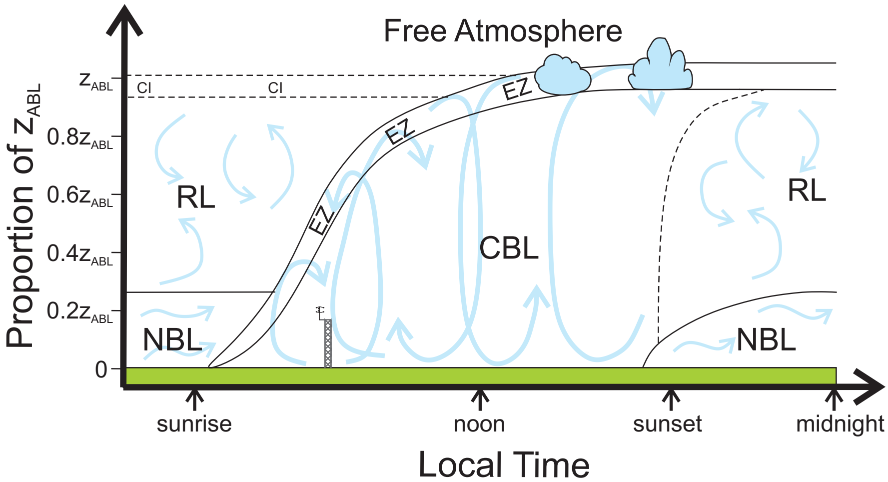

Figure 3: Idealized diel evolution of atmospheric boundary layer (adapted from Stull (1988)). z_{ABL} = daytime boundary layer height. NBL = Nocturnal boundary layer. RL = residual layer. CI = capping inversion. EZ = entrainment zone. CBL = convective boundary layer. Modified after Stull (1988).

hour or less, whereas the atmosphere above the ABL, called free atmosphere, is less sensitive to the surface interactions. Typically during daytime the ABL extends to a few thousands of meters above the surface, whereas the night time ABL is shallower (few hundreds of meters, or lower) (see Fig. 3).

At daytime the air flow in the ABL is almost always turbulent and the flow consist of mean flow and turbulent swirls, called eddies. The turbulence can be produced via two pathways: 1) mechanical production and 2) thermal production. Wind shear within the ABL is caused by the surface drag and the vertical gradient in wind speed produces turbulence (mechanical production). Solar heating increases air temperature close to the Earth's surface and, since warm air is more buoyant than cold air, the air column is unstable, the warm air starts to rise and turbulence is generated (thermal production). On the other hand, surface cooling can create stable layers (cool air below, warm air above) which inhibit vertical turbulent motions. Within the ABL, bulk of the transport of atmospheric constituents is caused by turbulence, unlike in the free atmosphere where the mean flow (i.e. advection) is the main transport mechanism. Molecular diffusion is important only within few millimetres above the surface.

The turbulent eddies are usually divided into three categories based on their size: the energy-containing range, the inertial subrange and the dissipation range. The production of turbulence takes place at the energy-containing range which consists of the largest eddies (up to the size of the ABL). The eddies are broken down to smaller scales at the inertial subrange, however turbulent energy is neither dissipated or produced at this size scale. At the smallest eddy size scale ($\sim$ millimeters) the kinetic energy of the turbulent eddies is dissipated by viscosity into heat. This transport of energy from the energy producing macroscale into the energy dissipating microscale is called the turbulent energy cascade (Kaimal and Finnigan, 1994).

The daytime ABL is often divided into three layers: the surface layer, the convective mixed layer and the entrainment zone (or capping inversion). The surface layer is the lowest 10 % of the boundary layer where the turbulent motions scale with height above ground and wind speed (U), potential temperature (θ) and gas concentration (c) exhibit approximately logarithmic vertical profile due to the immediate presence of the surface. Within the convective mixed layer, the large convective motions force a near-constant profiles of U, θ and c and the distance from the surface is not any more the main governing parameter of turbulent flow. The convective mixed layer is topped by the entrainment zone (i.e. capping inversion) which separates the free atmosphere from the ABL. The entrainment zone is characterised by a strong stable layer which inhibits turbulent motions and thus acts as a lid on the top of the ABL.

Nocturnal boundary layer (NBL) is usually characterised by stable stratification, low wind speed and intermittent turbulent mixing. Residual layer (RL) is located on top of the NBL, which is a leftover of the ABL developed during the previous day. During the morning hours the ABL grows, since the large convective eddies penetrate through the stable layer into the free atmosphere and entrain air into the ABL (Fig. 3).

2.2 Eddy covariance technique

The EC method for estimating the ecosystem scale surface exchange of scalar c is based on conservation of mass (Foken et al., 2012). Two assumptions are made in order to simplify the mass balance equation: 1) the turbulence and surface characteristics are horizontally uniform, i.e. there are no abrupt changes in surface roughness (for instance forest edges) or surface fluxes (for instance energy fluxes from lakes vs. nearby forest) and that 2) the turbulence is stationary, i.e. there are no time-dependence in turbulence statistical characteristics. After these assumptions, the mass balance equation is reduced to

$$\frac{\overline{\rho_d}}{M_d}\frac{\partial\overline{\chi_c}}{\partial t} = \frac{1}{M_d}\frac{\partial\overline{\rho_d}\overline{w'\chi_c'}}{\partial z}, \tag{1}$$

where ρ_d and M_d are the dry air density and molar mass, respectively, χ_c is the dry mole fraction of gas c and $\overline{w'\chi_c'}$ is the vertical turbulent flux of gas c. Overlines represent temporal averaging and the primes (') perturbations from the means. If Eq. 1 is integrated from the surface up to height z_m and the terms are slightly reorganised, the following equation is achieved:

$$F_c = \frac{\overline{\rho_d}}{M_d}\overline{w'\chi_c'}(z_m) + \int_0^{z_m}\frac{\overline{\rho_d}}{M_d}\frac{\partial\overline{\chi_c}}{\partial t}dz \equiv F_c^{EC} + F_c^{STO}, \tag{2}$$

where F_c is the surface flux of gas c, F_c^{EC} is the vertical turbulent flux acquired with EC and F_c^{STO} is the so-called storage change term, which takes into account any changes in $\overline{\chi_c}$ below the flux measurement level z_m (Foken et al., 2012).

In order to estimate the vertical turbulent flux, the turbulent air motions (i.e. wind) and gas mole fraction need to be measured. Generally, the three wind components (two horizontal, u and v and vertical, w) are measured with a sonic anemometer and the gas concentration is measured with an accompanying gas analyser, either an open-path which employs an open measurement cell or a closed-path which is connected to a sampling system (i.e. filters, tube and a pump). The measurements should be able to capture all the turbulent fluctuations (i.e. w' and χ_c') inflicted by different eddy sizes. The importance of different eddy sizes depends on height above surface and the prevailing mixing conditions, however an established practical solution has been to measure with 10 Hz sampling frequency and to calculate fluxes with 30-min time step, which corresponds approximately to 0.0006 Hz. Most of the turbulent exchange in the surface layer is within the range set by these two frequencies, while the conditions stay stationary within this averaging interval (Moncrieff et al., 2004). Once the measurements have been conducted, the covariance $\overline{w'\chi_c'}$ can be calculated simply as

$$\overline{w'\chi_c'} = \frac{1}{N}\sum_{i=1}^{N}\left(w_i - \overline{w}\right)\left(\chi_{c,i} - \overline{\chi_c}\right) = \frac{1}{N}\sum_{i=1}^{N}w_i'\chi_{c,i}', \tag{3}$$

where N is the amount of datapoints within an averaging period (typically $N = 18000$, due to 10 Hz sampling frequency and 30 min averaging period).

The source area of the vertical turbulent flux (i.e. the flux footprint) is generally estimated using models which are based on some assumptions and parametrisations of the boundary layer mixing (Rannik et al., 2012). The simple analytical models are valid only within the surface layer above a uniform surface, since they rely on surface layer scaling laws (e.g. Kormann and Meixner, 2001; Hsieh et al., 2000), whereas some models (or their parameterisations) based on Lagrangian stochastic dispersion modelling are applicable also outside this layer (e.g. Kljun et al., 2002, 2004). In theory, the footprint extends to infinite distance from the tower, mostly in the prevailing wind direction. The footprint function has a distinct peak at certain distance from the tower and the values decrease rapidly with distance from this peak (Rannik et al., 2012). In practice, the source areas are evaluated by examining different percentile curves of the footprint function, i.e. areas within which a certain percent (e.g. 80 %) of the turbulent flux originated from. The size of the footprint depends on measurement height, atmospheric stability, and in general on the surface properties and mixing conditions in the ABL (Rannik et al., 2012). See Fig. 2 for approximate ranges for short and tall flux tower footprints.

2.2.1 Random and systematic uncertainties in EC measurements

In reality, the measured EC flux ($F_c^{EC,meas}$) does not directly represent the "true" vertical turbulent flux (F_c^{EC}), since like any other quantity derived from measurements it contains random (δ) and systematic (Δ) uncertainty:

$$F_c^{EC,meas} = F_c^{EC} + \delta + \Delta \tag{4}$$

The random uncertainty stems from the fact that a finite sample of a stochastic process (turbulence) is used to estimate the flux. The consecutive samples in a turbulent time series (i.e. w' and χ_c') are not statistically independent of each other, since the turbulence stays correlated with itself over a certain period of time (integral time scale) (Lenschow et al., 1994) and this needs to be accounted for when δ is estimated. An additional source of random uncertainty is the instrumental noise. Finkelstein and Sims (2001) introduced a robust method to estimate the total random uncertainty of the vertical turbulent flux, whereas a separate estimate of the instrumental noise can be acquired using an approach by Lenschow et al. (2000).

The systematic uncertainties of the EC fluxes have gained wide attention in the scientific community and to date several sources of bias have been identified and procedures for correcting them have been developed (Aubinet et al., 2012). However, different correction procedures designed to correct the same bias often have a slightly deviating effect on the flux and to date no common set of data processing routines has been established, although this is what European and North American measurement networks (ICOS (Integrated Carbon Observation System) and NEON (National Ecological Observatory Network)) are currently striving for. Furthermore, even the same processing routine implemented in two processing software packages may produce slightly different result due to differences in the implementation of the method (Mauder et al., 2008; Fratini and Mauder, 2014). In the next section some of the commonly used data processing routines are presented.

2.2.2 EC data processing scheme

The systematic uncertainties mentioned above stem mainly from the limitations set by the measurement devices and/or setup. However, by carefully processing the data, EC fluxes can be inferred to be representative of the "real" vertical turbulent flux, i.e. the effect of all the biases can be corrected. Next, often used EC CH_4 data processing procedures are briefly presented, see also Fig. 4 (for a thorough review of EC data processing procedures, see e.g. Aubinet et al. (2012)):

1. Despiking Raw 10 Hz time series may contain spurious spikes resulting from signal degradation when it is transported from the analyser to the data logging machine and these spikes need to be removed.

2. Coordinate rotation The anemometer coordinate frame need to be rotated to correspond to the mean streamlines (Finnigan et al., 2003; Wilczak et al., 2001).

3. Detrending/Mean removal The turbulent signal (e.g. w') need to be separated from the measured signal (w) (Finnigan et al., 2003).

4. Time lag adjustment Any time delay between w' and χ_c' caused by the sampling system need to be accounted for prior to calculating the covariance $\overline{w'\chi_c'}$.

5. Spectral corrections Finite frequency response of the analysers and the sampling system and displacement of sensors attenuate the signal at high frequencies (Moncrieff et al., 1997; Eugster and Senn, 1995; Ibrom et al., 2007; Horst and Lenschow, 2009), whereas low frequency signal is dampened by limited averaging period and the methods used to separate the turbulent signal (e.g. χ_c') from the measurements (χ_c) (Rannik and Vesala, 1999). This attenuation of signal is usually corrected by determining transfer functions which describe the attenuation phenomena either based on theoretical (Moncrieff et al., 1997; Rannik and Vesala, 1999) or experimental approaches (Eugster and Senn, 1995; Ibrom et al., 2007; Mammarella et al., 2009), although different approaches do exist (e.g. Fratini et al., 2012; Nordbo and Katul, 2013).

6. Density (WPL) corrections Some analysers report molar density or wet mole fraction instead of dry mole fraction. Such measurements are affected by fluctuating water vapour and temperature (molar density) (Webb et al., 1980) or only by the water vapour fluctuations (wet mole fraction) (Ibrom et al., 2007). This can be corrected with the so-called density (WPL) correction (Webb et al., 1980). For data measured with a closed-path gas analyser this gives the same end-result as conversion of raw data to dry mole fraction, whereas for open-path data the correction can be done only on covariance level. Also, measurements with closed-path instruments are not affected by temperature fluctuations, since they are effectively dampened in the sampling tube (Leuning and Judd, 1996; Rannik et al., 1997).

7. Spectroscopic correction For gas analysers based on laser absorption spectroscopy (LAS), which do not report dry mole fractions, an additional spectroscopic correction is needed which accounts for the effect of temperature and water vapour on the absorption line shape used to estimate the gas concentration (McDermitt et al., 2011; Rella, 2010, **Paper II**).

Generally applied data processing steps are illustrated in Fig. 4 for two different types of gas analysers and their approximate relative magnitude for CH_4 fluxes are also shown. It must be noted however, that the relative magnitudes of each data processing step are somewhat measurement site/setup specific. The reported values describe situations when CH_4 fluxes are small (5 nmol m^{-2} s^{-1}) to moderate (20 nmol m^{-2} s^{-1}).

An EC data processing software called EddyUH has been developed by the Micrometeorology Group at the Department of Physics, University of Helsinki and it is an integral part of this thesis. The software contains most of the data processing routines found in the literature and it is cross-compared against another widely used software in **Paper III**, whereas in the other sections of this thesis (**Papers, I, II, IV**) it was used to process the EC data. Coding of EddyUH was originally motivated by the fact that the research group was running several EC sites and separate sets of codes were used at each one of them. In order to harmonize data processing, EddyUH was created. Later the software product has been made publicly available, so that also other scientists have more EC processing program alternatives from which to choose from.

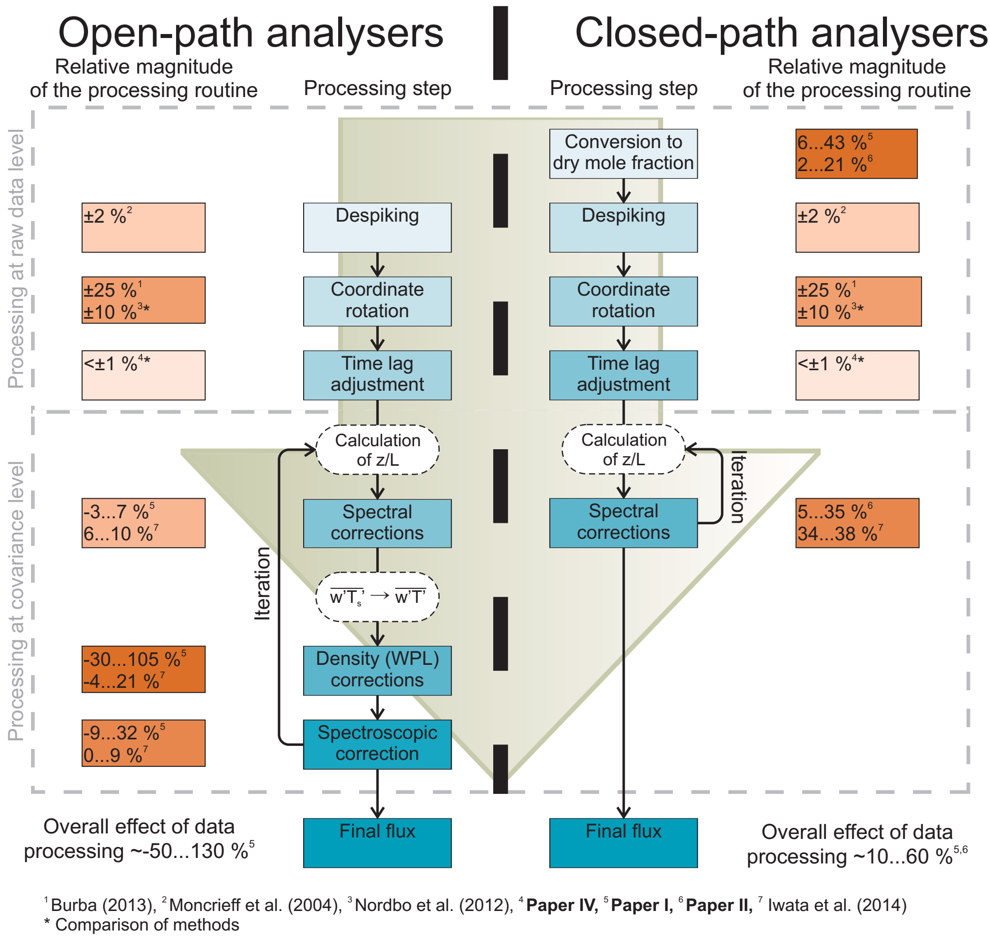

Figure 4: EC data processing scheme for open-path (left side) and closed-path (right side) gas analyser data. The relative significance of each processing step is given in the brown boxes (magnitude = shading) and they describe the processing of CH_4 fluxes (Negative values = correction increases downward fluxes, positive values = correction increases upward fluxes). White cylinders show processing steps which have an indirect effect on the CH_4 flux. Figure was modified from **Paper III**.

2.2.3 Special considerations when conducting flux measurements at tall towers

It has been established that the vertical turbulent fluxes show approximately linear decrease within the ABL (e.g. Stull, 1988):

$$\frac{F_c^{EC}(z)}{F_c} = 1 - \left(1 - \frac{F_c^{EC}(h)}{F_c}\right)\frac{z}{h}, \tag{5}$$

where $F_c^{EC}(z)$ is the vertical turbulent flux of c at height z, F_c is the effective surface flux, $F_c^{EC}(h)$ is the flux at the top of the ABL (entrainment flux) and h is the height of the ABL. $F_c^{EC}(h)$ is caused by the entrainment processes which take place at the top of the ABL. Close to the surface $F_c^{EC}(z)$ alone is relatively good approximation of the surface flux (cf. Eq. 5), whereas higher above the surface this is not always the case (**Paper IV**). Furthermore, decoupling between the surface and air layers above in stably stratified flows (e.g. Alekseychik et al., 2013) may potentially be more harmful for flux measurements high above the surface. However, as derived in Sect. 2.2, in theory the sum of the vertical turbulent flux and the storage change term is constant with height.

The ratio of entrainment flux and the flux at the surface ($F_c^{EC}(h)/F_c$) varies between scalar fluxes and it evolves throughout the day, depending on the status of the ABL (Huang et al., 2011). For instance, for heat flux $F_c^{EC}(h)$ is generally a few tens of percentages in magnitude of F_c (e.g. Stull, 1988), whereas for CO_2 flux during morning periods it can be up to three to five times larger than the surface flux (Casso-Torralba et al., 2008; de Arellano et al., 2004). For CH_4 flux the behaviour of this ratio is yet to be determined, although **Paper IV** touches on this issue.

2.3 Analysers based on laser absorption spectroscopy

The atmosphere contains only small trace amounts of CH_4 (global average concentration in 2011 was 1803 ppb (Hartmann et al., 2013)) and thus high precision instruments are needed in order to detect the mole fraction of this gas constituent. Therefore, the technology used in measuring CO_2 (Nondispersive infrared (NDIR) sensors) is not applicable for CH_4 measurements and more precise instruments based on tunable diode laser absorption spectroscopy (TDLAS) are needed. TDLAS analysers rely on precise determination of the shape of a particular absorption line which occur at certain frequencies (e.g. Werle, 1998), whereas NDIR analysers determine the absorption from a wider frequency range. Absorption lines are related to molecules' ability to absorb radiation at certain distinct frequencies and the strength and shape of an absorption line is related to the gas concentration via Beer-Lambert law. Generally, the strongest absorption lines of atmospheric constituents, including CH_4, reside in the mid-IR region (e.g. Werle, 1998).

The analysers used in atmospheric research of CH_4 apply lasers which function at the near-IR (e.g. telecom lasers) or mid-IR (e.g. lead-salt diode and quantum cascade lasers (QCL)) region (e.g. Crosson, 2008; Werle, 1998). The pioneering EC CH_4 studies in the early 1990's (e.g. Fan et al., 1992; Edwards et al., 1994) applied mid-IR lasers, which needed to be operated in cryogenic temperatures achieved with liquid nitrogen and were interfered by optical fringes which added noise to the signal (Werle, 1998). Furthermore, the instruments were highly unstable and not well-suited for rugged field conditions.

Since then, thermoelectrically cooled QCLs operating in room temperature have been developed (Nelson et al., 2004; McManus et al., 2010) and signal enhancing techniques, such as cavity-ringdown spectroscopy (O'Keefe and Deacon, 1988), integrated cavity output spectroscopy (O'Keefe, 1998) and wavelength or frequency modulation techniques (Silver, 1992) have allowed the usage of also the near-IR lasers for atmospheric research. In addition, the instrument stability and field performance have been improved and thus EC CH_4 studies have become common (cf. Fig. 1). To date several companies, such as Aerodyne Research Inc. (Nelson et al., 2004), Los Gatos Research (Baer et al., 2002), Picarro Inc. (Crosson, 2008) and LI-COR Biogeosciences Inc. (McDermitt et al., 2011) are producing instruments suitable for EC CH_4 measurements.

2.4 CH_4 production and emission to the atmosphere

The flux measurements included in this thesis were conducted in two different types of peatlands (pristine boreal fen (**Papers I, III**) and agricultural temperate peatland (**Papers II, IV**)), although urban fluxes were also included in **Paper III**. Wetlands are considered as the biggest source of CH_4 to the atmosphere, by emitting 177–284 $Tg(CH_4)\ yr^{-1}$ globally (excluding freshwaters and rice cultivation) (Ciais et al., 2013).

CH_4 is produced in anaerobic zones of submerged soils by methanogenic bacteria during the anaerobic digestion of organic matter (Le Mer and Roger, 2001) (cf. Fig. 5). On the other hand, CH_4 is also consumed in the oxic zones of the soil by the methanotrophic bacteria (Le Mer and Roger, 2001) and the net flux to the atmosphere from a given ecosystem is a balance between these two processes. Often, only a fraction of the produced CH_4 in the anoxic zone is eventually emitted to the atmosphere, since significant part of the CH_4 produced is oxidized while it is transported through the oxic zone (Le Mer and Roger, 2001).

The most important drivers for the CH_4 flux have been identified to be soil temperature (e.g. Christensen et al., 2003; Rinne et al., 2007; Yvon-Durocher et al., 2014), water table level in the soil (Christensen et al., 2003; Hendriks et al., 2010; Lai et al., 2014; Waddington and Roulet, 1996), availability of microbial substrates (Christensen et al.,

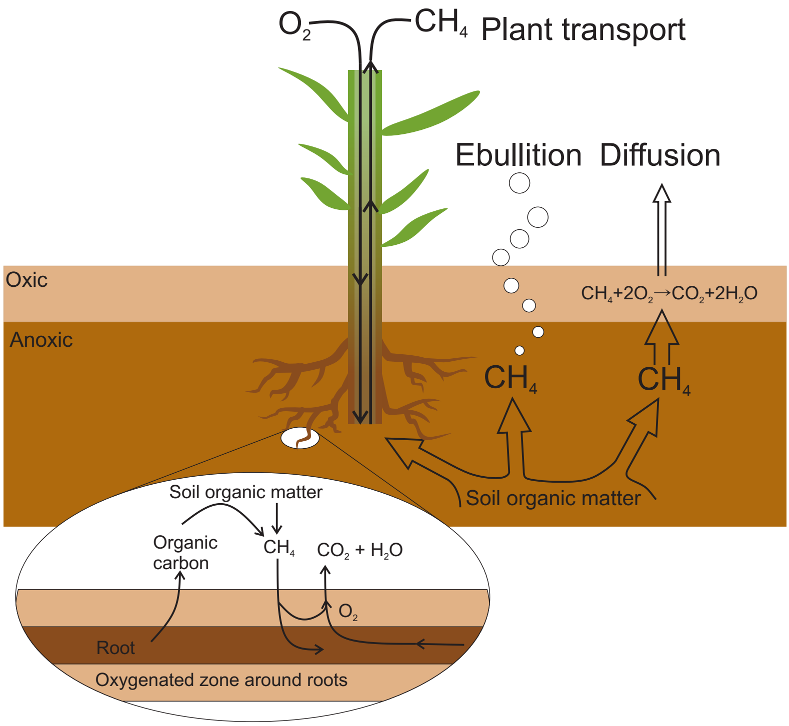

Figure 5: Schematic figure of CH_4 production, oxidation and transport pathways from a wetland with aerenchymatous vegetation (redrawn after Whalen (2005)).

2003) and the presence of aerenchymatous plant species (Hendriks et al., 2010; Lai et al., 2014). Water level has been found to be an on-off switch for CH_4 emissions (Christensen et al., 2003; Lai et al., 2014). Lai et al. (2014) suggested that this is partly due to the fact that in low water level conditions the plant roots do not reach down to the anoxic zone and thus the input of labile carbon from root exudates is not available for the methanogens to be used in methanogenesis. In addition, in the low water level situation the CH_4 oxidation in the soil is enhanced.

In wetlands, the CH_4 can be transported from the anoxic submerged soil to the atmosphere through the aerenchyma of aquatic plants (Kim et al., 1999; Henneberg et al., 2012; Schäfer et al., 2012; Hendriks et al., 2010), diffusion through the soil column or as bubbles, i.e. ebullition (Tokida et al., 2007; Goodrich et al., 2011; Klapstein et al., 2014) (Fig. 5). The three transport paths may co-occur simultaneously in a wetland and thus deducing their relative significance is difficult. Furthermore, for instance the flux related to ebullition may be decorrelated from the environmental forcing due to the interaction between bubbles and the peat structure, further hindering the analysis of these fluxes (Ramirez et al., 2015). Another example of the decorrelation between the observed CH_4 flux and the drivers of CH_4 production are the wintertime CH_4 emissions (e.g. Rinne et al., 2007), since the production in winter can be expected to be low. The aerenchymatous plants may transport CH_4 either passively via diffusion (Henneberg et al., 2012; Schäfer et al., 2012) or actively via convective throughflow (Kim et al., 1999; Hendriks et al., 2010) in the aerenchyma. While the plants generally increase the CH_4 flux to the atmosphere due to this transport route, they also create oxic pockets around their roots in the anoxic soil where thereby CH_4 oxidation can take place (Le Mer and Roger, 2001) (Fig. 5).

Generally, due to the spatial variability of either the CH_4 production drivers or the transport paths, the flux exhibits significant variability within an ecosystem (Waddington and Roulet, 1996; Riutta et al., 2007; Hendriks et al., 2010; Schrier-Uijl et al., 2010a,b; Teh et al., 2011). Thus in order to produce defensible CH_4 budgets which represent large areas, the fluxes should be measured with methods which integrate over large areas (O'Shea et al., 2014; Desai et al., 2015; Winderlich et al., 2014, **Paper IV**), or alternatively high resolution spatial maps of the CH_4 flux driving variables should be created which then could be used to upscale chamber measurements (Riutta et al., 2007; Schrier-Uijl et al., 2010a; Forbrich et al., 2011; Teh et al., 2011).

3 Sites and measurements

In this thesis, data from two contrasting peatland sites were used. The first one is a pristine fen in Southern Finland and the second one is an intensively managed agricultural peatland in the Netherlands.

3.1 Siikaneva

Siikaneva is a pristine open boreal fen (Fig. 6) located in Southern Finland (61°50'N, 24°12'E, 162 m a.s.l.). The study site is a nutrient poor, i.e. oligotrophic, fen and the vegetation at the site consist mostly of mosses (*Sphagnum balticum* (Russow) C.E.O Jensen, *S. majus* (Russow) C.E.O Jensen, *S. papillosum* Lindb.), sedges (*Carex rostata* Stokes, *C. limosa* L., *Eriophorum vaginatum* L.) and rannochrush (*Scheuchzeria palustris* L.). The site has fairly flat topography, with no apparent slope or string-hollow structures. The open relatively uniform fetch extends about 200 m North and South of the EC tower and several hundreds of meters to the East and West (see the inset in Fig. 6). Based on Riutta et al. (2007) in typical conditions the 75th percentile of the footprint extended to 200 m distance from the tower, that is 75 % of the flux signal originated closer than this distance. Peat depth at the site varies between 2 m and 4 m meters. The average summertime CH_4 emission measured during 2005 at the site by Rinne et al. (2007) was approximately 60 nmol m^{-2} s^{-1}. Based on Rinne et al. (2007) the emissions started to increase from the lower wintertime values ($\sim$ 4 nmol m^{-2} s^{-1}) at mid-May and they peaked at July-August ($\sim$ 72 nmol m^{-2} s^{-1}). See Rinne et al. (2007) and Riutta et al. (2007) for further details of the site.

To address the specific aim 1) above, a CH_4 instrument intercomparison campaign was held between 1st of April and 26th of October 2010 at the site. In addition to the four CH_4 analysers included in the study (Table 1), a three-axis sonic anemometer (USA-1, METEK GmbH., Germany) was used to acquire the three wind components and sonic temperature and LI-7000 (LI-COR Biogeosiences, USA) was used to measure CO_2 and H_2O. The sonic anemometer was located 2.75 m above ground and the gas analysers were sampling from below the anemometer (cf. Fig. 6). In addition to the Siikaneva CH_4 intercomparison study (**Paper I**), LI-7700 and G1301-f data were used also in the cross-comparison of EC processing software programs (**Paper III**) in order to address the specific aim 2) of this thesis. For further details of the EC setup, see **Paper I**.

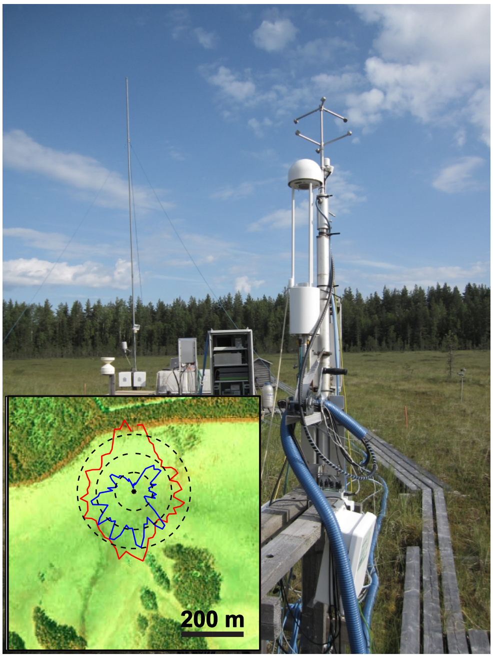

Figure 6: The EC measurement setup used in the Siikaneva intercomparison study (**Paper I**) and in the cross-comparison of processing software packages (**Paper III**) (photo: Sami Haapanala). The inset shows aerial picture of the site (light green = fen, dark green = surrounding forest). Red line shows CH_4 flux magnitude and the blue line shows the amount of flux data in different wind directions. Dashed lines show where CH_4 flux equals 17, 35 and 52 nmol m^{-2} s^{-1} and the amount of data equals 60, 120 and 180 points.

3.2 Cabauw

The Cabauw Experimental Site of Atmospheric Research (CESAR, 51°58'12.00"N, 4°55'34.48"E, -0.7 m a.s.l) is located in the "Groene Hart" (i.e. Green Heart) of the Netherlands. The area is relatively sparsely populated and largely used for agriculture when compared to other parts of the Netherlands. Detailed descriptions of the site have been given by Beljaars and Bosveld (1997) and Van Ulden and Wieringa (1996). The landscape is dominated by rectangular field patches separated by drainage ditches which are used to control the water level in the soil (cf. Fig. 7). The field areas are mainly intensively managed grasslands (dominant grass species: *Lolium perenne* L., *Poa trivialis* L., *Alopecurus geniculatus* L.) used as pasture, or for growing hay or livestock fodder. The farms in the area are mainly dairy farms (see **Paper IV** for livestock statistics). The area is flat with no apparent slopes and vegetation height is generally below 1 m. The soil consists mostly of river clay and peat (top 0.6 m: mostly clay, 0.6–0.75 m: mixture of clay and peat, 0.75–7.00 m: peat) and most of the roots are at the top 0.18 m deep soil layer (Jager et al., 1976). The water level in the soil is actively monitored in several locations in the area and it is on average about 0.4 m below the surface (Beljaars and Bosveld, 1997). The drainage ditches and ditch edges are CH_4 emission hotspots, whereas the central parts of the fields are not as significant emitters of CH_4 (Hendriks et al., 2010; Schrier-Uijl et al., 2010b). There are two slightly larger towns in the area: Lopik (pop. 5500, 0.9 km to the east from CESAR) and Schoonhoven (pop. 11900, 5 km to the southwest from CESAR). However, they had negligible influence on the flux measurements.

The Cabauw measurement campaign consisted of two parts: CH_4 instrument intercomparison (**Paper II**; between 6 and 27 June 2012) and CH_4 flux spatial variability study (**Paper IV**; between 1 and 25 July 2012). CH_4 analysers used are shown in Table 1. In the first part of the campaign all the analysers were measuring at the same location for three weeks (see specific aim 1) of this thesis) and in the second part these analysers were spread around the landscape in order to study the CH_4 flux variability and tall tower fluxes (specific aims 3) and 4)). The Cabauw area was selected for this particular campaign mainly due to two reasons: 1) CESAR site has an excellent infrastructure (e.g. over 200 m tall tower) which allowed easy implementation of the campaign measurements and 2) CH_4 emitting peatlands cover several square kilometers around the CESAR site. In the first part, two sonic anemometers were utilized (both USA-1, METEK GmbH., Germany) to acquire the wind and air temperature data. Also LI-7500 and LI-7000 (LI-COR Biogeosciences, USA) were used to measure CO_2 and H_2O concentrations. In the second part the USA-1 anemometers were operated at the CESAR 6 m and Temporary site 1 locations, whereas at the CESAR 20 m and Temporary site 2 Windmaster Pro (Gill Instruments Ltd, UK) sonic anemometers were utilized and at the CESAR 60 m R3-50 (Gill Instruments Ltd, UK) sonic anemometer was used. Additionally, at the Temporary site 1 LI-7000 was employed to measure CO_2 and H_2O. For a more thorough description, see **Papers II** and **IV**.

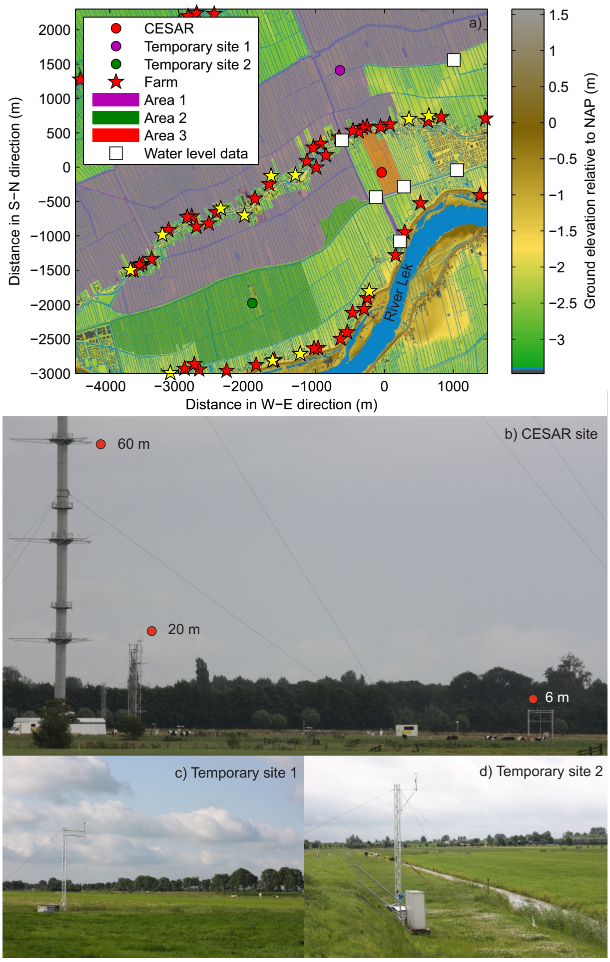

Figure 7: Overview of the experimental setup at the CESAR site in Cabauw, the Netherlands. The colour in the topmost plot (a)) shows the ground elevation (dark grey: buildings/elevation data not available;blue: water surface) relative to Normal Amsterdam Level (NAP) (AHN-2, www.ahn.nl). Yellow stars show farms with more than 100 cows. Water level in the ditches was controlled in areas 1, 2 and 3 separately from each other. See **Paper IV** for further figure details. Study presented in **Paper II** was conducted at the CESAR site 6 m tower, whereas all five measurement locations were employed in **Paper IV**.

Table 1: CH_4 instruments used in this thesis. Roman numerals refer to the papers in which the instruments were used. Picarro = Picarro Inc., USA, LGR = Los Gatos Research, USA, Aerodyne = Aerodyne Research Inc., USA, LI-COR = LI-COR Biogeosciences, USA, Campbell = Campbell Scientific, USA

Model	G2311-f	G1301-f	FGGA	FMA	pQCL	LI-7700	TGA-100A
Manufacturer	Picarro	Picarro	LGR	LGR	Aerodyne	LI-COR	Campbell
Production year	2011	2009	2008	2005-2008	2005	2009[a]	2003
I		x		x[b]		x[c]	x
II	x	x	x	x[d]	x	x	
III		x				x[c]	
IV, CESAR 6 m	x						
IV, CESAR 20 m		x		x			
IV, CESAR 60 m			x				
IV, Temp. site 1				x			
IV, Temp. site 2				x			

[a] Estimate
[b] Called RMT-200 in **Paper I**
[c] A prototype of later commersialised LI-7700 was used.
[d] Three different FMAs were included of which one was retrofitted to measure also H_2O and one was a benchtop model (called DLT-100 in **Papers II, IV**).

4 Overview of key results

4.1 Random and systematic variation between EC CH_4 instrumentation

When comparing instruments, an important metric for the performance is the amount of noise in the outputted signal. Instrument comparisons were related to the specific aim 1) of this thesis (see Sect. 1). Two different approaches for estimating the random uncertainty were taken in the Siikaneva (**Paper I**) and Cabauw (**Paper II**) intercomparisons: in the former one the flux total random uncertainty (1-σ random uncertainty of the covariance) was estimated (Finkelstein and Sims, 2001), whereas in the latter one the instrumental noise (i.e. 1-σ white noise in the 10 Hz CH_4 data) was separated and estimated from the EC measurements (Lenschow et al., 2000; Mauder et al., 2013). The estimates for the instrumental noise varied significantly between the instruments (cf. Fig. 8a). The differences between noise levels reflect the age of the instruments: the Aerodyne pulsed-QCL (pQCL) was the oldest instrument, FGGA the newest of the Los Gatos analysers and the two Picarro analysers were newest analysers tested in the Cabauw campaign (cf. Table 1).

The instrumental noise did not however have a significant contribution to the flux random uncertainty: for the slightly newer analysers the relative flux uncertainty related to the instrumental noise was generally 5 % or less (cf. Fig. 8b). For the method how to translate the instrumental noise (in ppb) to the corresponding flux uncertainty, see

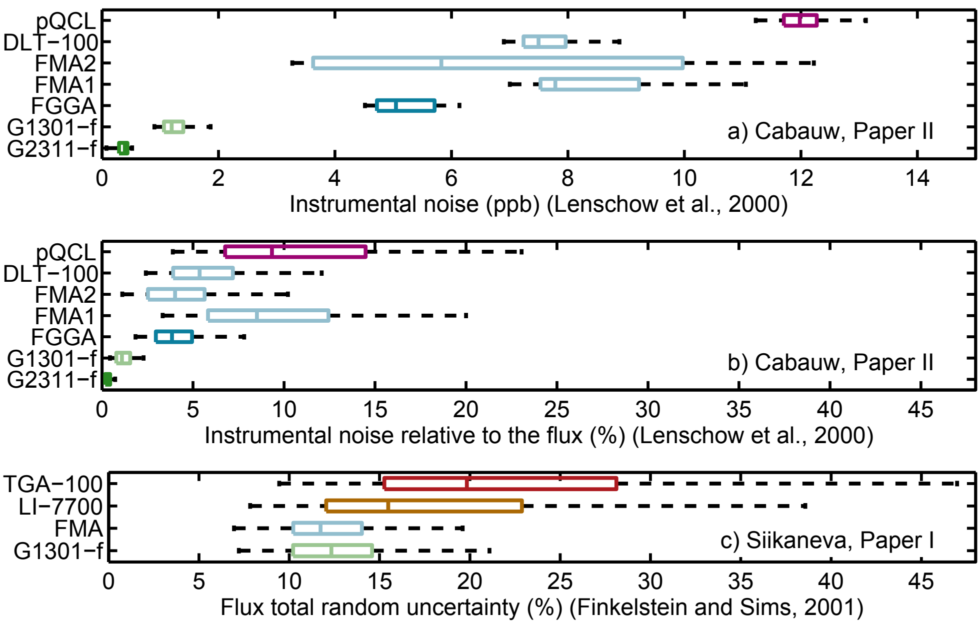

Figure 8: Boxplots of random uncertainty estimates obtained during the two instrument intercomparison campaigns held in Cabauw and Siikaneva (**Papers II** and **I**, respectively): (a) instrumental noise (i.e. 1-σ white noise in 10 Hz concentration time series) estimated with the method by Lenschow et al. (2000), (b) the noise relative to the flux and (c) the total flux random uncertainty (1-σ random uncertainty of the 30-min covariance) estimated with the method by Finkelstein and Sims (2001) are shown in the figure. The data shown in (b) and (c) were normalised with the corresponding flux values. See the instrument abbreviations in Table 1.

e.g. Mauder et al. (2013) or **Paper II**. Although the results showing the total random uncertainty of the flux in Fig. 8c are from another site than the results in Fig. 8b, they can still be qualitatively compared. It is evident from this comparison that the flux random uncertainty is dominated by stochastic variation of turbulence (Sect. 2.2.1) rather than the noise in the CH_4 analyser signal, at least when using relatively new analysers. Thus even relatively noisy signal of pQCL or TGA-100A did not prevent estimation of CH_4 fluxes from their measurements. However, turbulent flux varies several orders of magnitude (e.g. Fig. 6 & 7 in **Paper II**) depending on the eddy size and therefore e.g. estimation of the dampening of the high frequency end of the signal from the noisy data (cf. Sect. 2.2.2) may be difficult or even impossible. Therefore even though the direct effect of instrumental noise on the flux uncertainty is relatively small, the indirect effect e.g. via hindering spectral analysis may be more important. Consequently, instruments with as low noise levels as possible should be favoured.

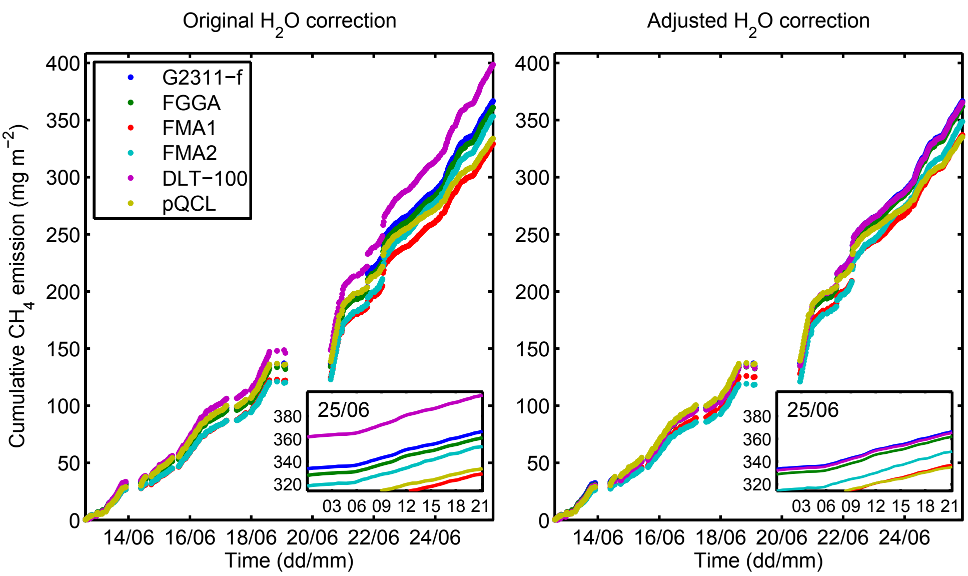

Figure 9: Cumulative sums of CH_4 fluxes during a part of the intercomparison campaign held in Cabauw (from 12 to 25 June). The time series were not gapfilled and they all contain the same amount of points so that it is possible to evaluate the spread between CH_4 flux measurements. The insets show a close-up of the last day. For the differences between H_2O corrections, see **Paper II** from where this figure was adopted.

Cumulative CH_4 emissions diverged from each other during the Cabauw campaign (Fig. 9, left plot), which suggests that there were systematic differences between the CH_4 fluxes. The cumulative fluxes ranged between 329 (FMA1) and 399 mg(CH_4) m^{-2} (DLT-100), whereas the spread between analysers which measured also H_2O in addition to CH_4 was smaller (353 (FMA2) and 367 mg(CH_4) m^{-2} (G2311-f)). It was concluded in **Paper II** that most of the divergence between cumulative CH_4 emissions was caused by incomplete H_2O corrections (i.e. corrections for the density (Webb et al., 1980; Ibrom et al., 2007) and spectroscopic effects (Rella, 2010)) and, after applying an *ad hoc* adjustment to the H_2O correction, the agreement between cumulative CH_4 fluxes was improved (Fig. 9, right plot). The overall variability between the cumulative CH_4 emissions with and without this *ad hoc* adjustment were 4 % and 7 % of the mean cumulative CH_4 emission, respectively. Also the cumulative emissions over a summer period (1 May to 25 October) in Siikaneva study (**Paper I**) calculated from gapfilled data agreed well (12.3 (FMA), 11.9 (G1301-f) and 11.8 g(CH_4) m^{-2} (TGA-100A)).

4.2 Critical steps when processing EC CH_4 data

The relative significance of different data processing steps are shown in Fig. 4. They were estimated in order to reach the specific aim 2) of this thesis (see Sect. 1). Evidently, careful data processing is more important for analysers based on open-path design than on closed-path design. The corrections combined may be over 100 % of the measured signal for open-path analysers (e.g. LI-7700) in relatively low flux conditions (Figs. 4 & 10c). CH_4 measurements with such analysers are susceptible to temperature and H_2O fluctuations since they cause air density fluctuations which, in turn, manifest themselves as CH_4 molar density fluctuations and therefore as apparent CH_4 flux. This well-known effect (density correction, also known as WPL correction) was first derived by Webb et al. (1980) and can be corrected accurately, since the correction is based on robust physical laws with minimal assumptions and/or approximations. However, as stressed in **Paper I** and also by Iwata et al. (2014) and Lee and Massman (2011), any bias in the measurements used in the correction will also inflict a bias to the CH_4 fluxes. In addition, since the correction is additive rather than multiplicative, its relative size may increase significantly when the actual signal is small (as in Fig. 10).

Instruments based on closed-path design are not as vulnerable to the density fluctua-

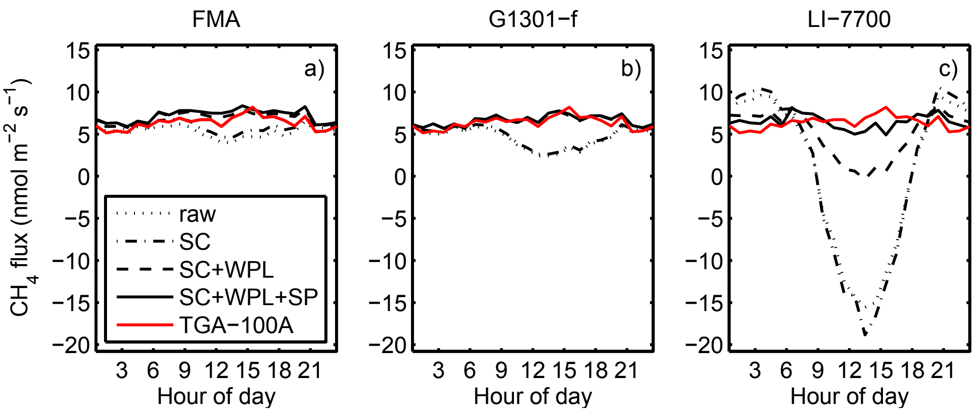

Figure 10: Diel patterns of CH_4 fluxes measured with different analysers at different stages of data processing. raw = raw covariance. SC = spectral corrections. WPL = density corrections. SP = spectroscopic corrections. Black lines show the final, fully corrected fluxes. Fully corrected TGA-100A fluxes are shown as reference. The figure was adopted from **Paper I**.

tions, since the temperature fluctuations are effectively dampened in the sampling tube (Leuning and Judd, 1996; Rannik et al., 1997) and the H_2O is dampened and partly desynchronized from CH_4 while it is transported in the sampling line (Ibrom et al., 2007; Nordbo et al., 2013, **Paper II**). However, due to these effects that the sampling line has on H_2O, the H_2O corrections (i.e. density and spectroscopic corrections) need to be executed with the H_2O data obtained with the same instrument which is used to measure CH_4 (Ibrom et al., 2007, **Paper II**). Some of the CH_4 analysers tested in the Cabauw intercomparison (**Paper II**) did not measure H_2O, and thus the H_2O corrections were done using H_2O measured with another instrument. This approach slightly biased the CH_4 fluxes and thus increased the divergence between cumulative CH_4 emissions (see Fig. 9 and the related discussion in Sect. 4.1).

For closed-path instrument the so-called spectral corrections are often thought to be more important, although in this study they were of similar magnitude as the H_2O corrections (cf. Fig. 4). The spectral corrections rectify for high and low frequency dampening of the signal (Moncrieff et al., 1997; Eugster and Senn, 1995; Ibrom et al., 2007; Rannik and Vesala, 1999). Most of the high frequency dampening is caused by the sampling line (i.e. tube and filters) and thus these corrections are usually smaller for fluxes measured with open-path gas analysers. Unlike the robust density correction, several different methods for correcting these losses have been developed (Moncrieff et al., 1997; Ibrom et al., 2007; Mammarella et al., 2009; Horst, 1997; Fratini et al., 2012; Nordbo and Katul, 2013). The theoretical approach (Moncrieff et al., 1997) has been deemed to be inaccurate (e.g. Nordbo et al., 2012, **Paper III**), but out of the experimental approaches (Ibrom et al., 2007; Mammarella et al., 2009; Horst, 1997; Fratini et al., 2012; Nordbo and Katul, 2013) none has emerged as superior over others.

While the relative importance of different EC data processing steps have been quantified before (e.g. Mauder et al., 2007, 2008; Nordbo et al., 2012), none of the studies have concentrated on CH_4 fluxes. The implementation of different corrections in two EC processing software programs, EddyUH and EddyPro®, were compared in **Paper III**. This was done in order to verify that the two software programs output similar results and thus to ensure that either one of the two is a viable alternative for EC processing. Closed-path (G1301-f) CH_4 fluxes from the two programs agreed well:

$F_{\mathrm{EddyPro}} = 1.00 F_{\mathrm{EddyUH}} - 0.13\ \mathrm{nmol\,m^{-2}\,s^{-1}}$, $r^2 = 0.999$, RMSE $= 0.77\ \mathrm{nmol\,m^{-2}\,s^{-1}}$,

where F_{EddyPro} and F_{EddyUH} are G1301-f CH_4 fluxes processed with EddyPro and EddyUH, respectively. However, slightly worse agreement was obtained for open-path (LI-7700) CH_4 fluxes:

$F_{\mathrm{EddyPro}} = 1.00 F_{\mathrm{EddyUH}} + 0.42\ \mathrm{nmol\,m^{-2}\,s^{-1}}$, $r^2 = 0.997$, RMSE $= 0.88\ \mathrm{nmol\,m^{-2}\,s^{-1}}$.

The two software programs have a somewhat different approach when estimating the high frequency dampening of the fluxes: EddyUH estimates the dampening by comparing $w\,CH_4$ cospectra with $w\,T$ cospectra, whereas EddyPro does the comparison using CH_4 and T power spectra. Here the T high frequency signal is thought to be undampened and used as a reference. When using power spectra for such an analysis, a separate correction for sensor separation induced dampening needs to be included (Horst and Lenschow, 2009), whereas analysis based on cospectra inevitably contains this source of dampening. It was shown in **Paper III** that this sensor separation correction in EddyPro weakened the agreement between CH_4 fluxes from different instruments and spectral corrections in general were the main reason why the agreement between LI-7700 CH_4 fluxes from the two software programs was worse than in the case of closed-path fluxes.

The agreement between long-term cumulative sums of non-gap-filled flux time series were used to assess systematic differences between the two software programs. Such a difference would cause bias in the long-term CH_4 balance. For closed-path G1301-f cumulative CH_4 flux the relative difference was negligible (0.03 %, EddyUH fluxes larger), whereas for open-path LI-7700 CH_4 cumulative fluxes a larger difference was found (-6.7 %, EddyUH fluxes smaller). If the additional sensor separation correction needed only in EddyPro was omitted, the agreement was slightly better (1.0 %, EddyUH fluxes larger), albeit still significant. This result highlights the significance of spectral corrections also in the case of open-path analysers and further that the sensor separation should be minimized when using open-path analysers close to the ground, where small eddies dominate the transport (**Paper III**).

4.3 Spatial variability of EC CH_4 fluxes in an agricultural peatland landscape

In order to reach the specfic aim 3) of this thesis, spatial variability of EC CH_4 fluxes were estimated in **Paper IV** with three short EC towers spread around the Cabauw landscape (cf. Fig. 7). In previous studies (e.g. Waddington and Roulet, 1996; Riutta et al., 2007; Hendriks et al., 2010) the variability has been studied at the plot scale ($\sim$ 1 m^2), although one other multi-tower study does exist (Matthes et al., 2014). CH_4 fluxes from the three sites deviated from each other (medians: 30 nmol m^{-2} s^{-1} at the Temporary site 1; 24 nmol m^{-2} s^{-1} at the Temporary site 2; 36 nmol m^{-2} s^{-1} at the CESAR 6 m). The differences between sites were significantly higher than the differences between instruments observed in the **Paper II**. Also, a diel pattern (higher fluxes at daytime and lower at night time) in the CH_4 flux was observed at one site (CESAR 6 m), whereas at the other two sites CH_4 fluxes did not contain a diel course. These findings suggest that there were differences in either CH_4 production, oxidation and/or transport paths from the soil to the atmosphere between the sites.

For CH_4 fluxes, the spatial variability (σ_{spa}) was of similar magnitude as the temporal variability (σ_{tem}), whereas for other fluxes measured at the three sites (sensible heat flux (H) and friction velocity ($u_\star$)) the spatial variability was an order of magnitude smaller than the temporal variability. The relative importance of these two sources of variability reflects the representativeness of EC measurements, since the σ_{tem} can be readily estimated from measurements at one short tower, whereas for estimating the σ_{spa} several towers are needed. This result was not surprising given the highly spatially variable nature of CH_4 flux (see Sect. 2.4 and references therein) and the fact that H

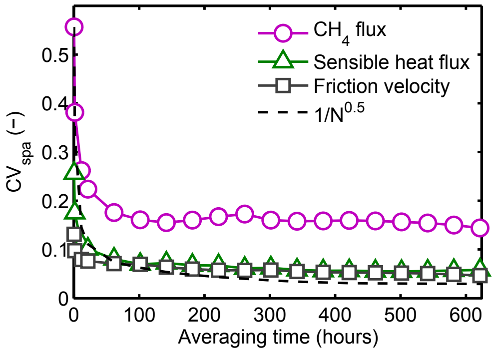

Figure 11: Coefficient of variation ($CV_{spa} = \sigma_{spa}/F$) as a function of time used in averaging the CH_4 flux time series prior to calculating the σ_{spa}. Dashed black line shows the expected decrease in CH_4 flux CV_{spa} if the spatial variability is related only to a random process. Adopted from **Paper IV**.

and $u_\star$ tend to have a clear diel pattern. The σ_{spa} of CH_4 flux was significantly higher than the σ_{spa} of H and $u_\star$ (Fig. 11). Similar result was found for CO_2 flux by Katul et al. (1999) and Oren et al. (2006): in their study the spatial variability was ranked as $u_\star < H < F_{CO_2}$.

The effect of temporal scale on spatial variability of the flux was evaluated by calculating the σ_{spa} from flux time series which were aggregated in time with varying averaging times (Fig. 11). This kind of analysis allowed studying the spatial variability of long-term CH_4 budgets and helped to assess whether the spatial variability is random or systematic, since random variation diminishes with averaging (relative to $1/\sqrt{N}$, where N is the amount of samples), whereas systematic does not. CV_{spa} (σ_{spa} normalised with the flux) decreased rapidly when the averaging time was increased, which corresponds to the decrease in random variation. However, at long averaging times the CV_{spa} plateaued (for CH_4 flux $CV_{spa} = 0.14...0.17$). This value characterises the systematic variability of CH_4 flux in this landscape and should be taken into account when estimating long-term (e.g. annual) CH_4 balances in similar environments. It was estimated in **Paper IV** that the spatial variability of CH_4 flux contributed up to 50 % of the uncertainty of annual CH_4 emission published elsewhere (Kroon et al., 2010).

4.4 Evaluation of tall flux tower EC system in measuring landscape scale CH_4 emissions

To address aim 4) the applicability of a tall tower EC system in measuring landscape CH_4 emission was evaluated by measuring fluxes also at two higher levels (20 m and

60 m above ground) during the second part of the Cabauw campaign (Fig. 7). This was done in order to study whether the tall flux tower measurements average out the spatial variability seen between the three short towers (Sect. 4.3), and thus providing a better estimate of the landscape level CH_4 flux. Systematically higher CH_4 fluxes were observed at the 60 m level than at lower levels, whereas 20 m fluxes were more comparable with the 6 m towers. Generally, the sum of the turbulent flux and the storage change term (Eq. 2) increased with height rather than stayed constant, and turbulent CH_4 flux did not follow a clear linear pattern with height, as it should in horizontally homogeneous situation (Sect. 2.2.3). 56 % of the difference between 60 m and 6 m CH_4 fluxes could be explained with bottom-up estimates of CH_4 emissions from nearby farms calculated using emission factors and footprint modelling (see the details in **Paper IV**). However, the difference between heights prevailed also in wind directions without direct farm emissions.

During some mornings the CH_4 fluxes at the three heights showed significant differences when the switch between stably stratified nocturnal boundary layer and the unstable convective boundary layer took place. Fig. 12 shows examples of two days when the CH_4 fluxes showed deviating patterns during these transition periods. CH_4 fluxes peak (at 60 m level up to 600 nmol m^{-2} s^{-1}) during the onset of convective mixing in the morning, whereas during the collapse of convective boundary layer in the evening the fluxes show spurious values. These findings can be attributed to the changes in boundary layer mixing and not related to changes in surface CH_4 flux. In order to the sum of turbulent flux and the storage change term accurately represent the surface flux (i.e. to be constant with height), the effect of entrainment on the vertical turbulent flux should be balanced by similar (but opposite sign) changes in the storage change term. This is a demanding requirement, especially when the entrainment flux is several times larger than the surface flux (Casso-Torralba et al., 2008; de Arellano et al., 2004). Despite these limitations that the tall tower EC measurements have, they were concluded in **Paper IV** to be the best option if the whole landscape scale exchange emissions are studied due to their ability to measure CH_4 exchange continuously, unattended, over extended periods of time.

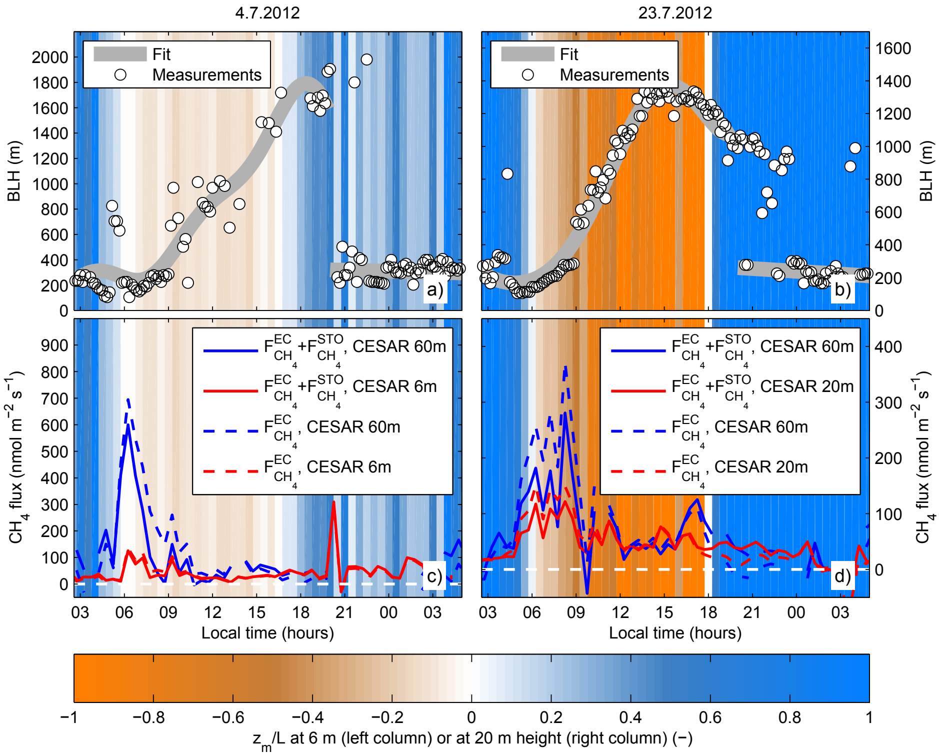

Figure 12: Examples from two days (4 and 23 July 2012) when the fluxes at the tall flux tower were not representative of the surface fluxes during the transition periods between night and day. The few boundary layer height (BLH) values around 600..800 m between 5:00 to 6:00 in 4.7.2012 are most likely related to the top of residual layer rather than the nocturnal boundary layer (see also Fig. 3). Note the changing scales on y-axes. The figure is found in **Paper IV**.

5 Review of papers and the author's contribution

The general aim of this thesis was to quantify the random and systematic uncertainties related to the ecosystem scale CH_4 emission measurements and finding ways to minimize the systematic uncertainties. The main aim was further divided into four parts (see Sect. 1). **Papers I** and **II** answer to the specific aim 1) and, together with **Paper III**, also to the aim 2). **Paper IV** covers the specific aims 3) and 4).

Paper I evaluates the performance of four EC CH_4 gas analysers during a summer field campaign held at Siikaneva fen. The instruments were measuring at the same location and the EC data were processed with the same set of codes (EddyUH). Thus discrepancies between the estimated fluxes could be linked to differences between instruments and furthermore they could be used to address the specific aim 1) of this thesis. Overall, good agreement between instruments was found and the cumulative CH_4 fluxes over the summer period were between 11.8 g(CH_4) m^{-2} and 12.3 g(CH_4) m^{-2}. However, we demonstrated that careful data processing was needed in order to acquire this result, since the flux corrections could be over 100 % of the originally measured signal (cf. aim 2)).

Paper II presents results from another CH_4 instrument intercomparison in which a comprehensive set of eight CH_4 analysers were cross-compared at a Dutch agricultural peatland (cf. aim 1)). A 10-fold difference between instrument noise was found, however the variability between cumulative CH_4 fluxes was only 7 % of the mean cumulative CH_4 emissions. The study has a special emphasis on H_2O corrections that are done to the CH_4 data (cf. aim 2)).

Paper III introduces EddyUH, a comprehensive software program for EC data processing. The software product was originally created to meet the needs of the Micrometeorology group at the University of Helsinki, but it was made also publicly available so that also other researchers can use it in their work. Various datasets and processing combinations were used and cross-compared with another EC software, EddyPro, and the results were shown to be in line between the software packages. We concluded that the biggest discrepancies between the software programs were related to spectral corrections (cf. aim 2)).

Paper IV investigates the spatial variability of EC CH_4 fluxes in an agricultural peatland landscape. This was the second study to evaluate the spatial variability of CH_4 fluxes by utilizing multiple EC towers. CH_4 fluxes varied spatially significantly more than the other studied fluxes and the variability was on the same order of magnitude as the temporal variability. This result has implications for spatial representativeness of EC CH_4 fluxes and thus for flux upscaling (aim 3)). We therefore evaluated also the suitability of tall flux tower EC measurements in providing more spatially aggregated flux estimates (aim 4)).

I am solely responsible for the introductory part of this thesis, for the raw data processing and for the final preparation of flux data for further analysis in all of the publications included in this thesis. I designed and carried out the data analysis in **Papers I**, **II** and **IV** and wrote the publications. The co-authors contributed by commenting the text and/or conducting measurements. I did part of the data analysis and writing of **Paper III**. The EC data processing software, EddyUH, has a big role in this thesis. I made the graphical user interface and approximately half of the data processing codes included in the software. In addition, I am updating the software when needed. Regarding field work, I participated in setting up the measurement system used in **Papers II** and **IV** and did altogether three weeks of field work in the Netherlands for the **Papers II** and **IV**.

6 Conclusions and outlook

During the last decade the EC CH_4 flux studies have become more common, mainly due to the rapid instrument development. This progress motivated this study which aimed to evaluate the random and systematic uncertainties in EC CH_4 measurements. Particularly three sources of systematic uncertainty were considered: variability between instruments, data processing software packages and the spatial variability of ecosystem scale ($\sim$ 1 ha) EC CH_4 fluxes. The related conclusions for the detailed aims outlined in Sect. 1 (also in italics below) are as follows:

1) *to quantify the random and systematic variation between EC CH_4 flux instrumentation*
The EC CH_4 analysers measured comparable CH_4 fluxes during the two intercomparison campaigns included in this thesis. However, an order of magnitude difference in noise was observed, which reflected the design year of the instruments: the new analysers were more precise. Nevertheless, the instrumental noise did not contribute significantly to the total flux random uncertainty which was dominated by the sampling uncertainty. Systematic differences were observed between the instruments and partly the deviations could be attributed to the incomplete H_2O corrections. Thus analysers which measure H_2O in addition to CH_4 should be used. The overall variability between the cumulative CH_4 emissions were 7 % (4 % with an *ad hoc* correction) of the mean cumulative emission, which demonstrated the systematic variability between the instruments.

2) *to assess the impact of different EC data processing routines on the CH_4 fluxes and to cross-compare the implementation of these routines between two data processing software products*
The data processing had a significant impact on EC CH_4 fluxes: for open-path analysers the corrections were often above 100 % of the originally measured flux and for closed-path analysers the corrections were usually between -10...60 %. Two eddy covariance data processing software programs (EddyUH and EddyPro) were cross-compared and their output agreed well for the closed-path CH_4 fluxes (0.03 % difference in cumulative CH_4 emissions, EddyUH fluxes higher), whereas differences were observed between the analysis of open-path fluxes (6.7 % difference in cumulative CH_4 emissions, EddyUH fluxes smaller). The deviations were mainly related to the spectral corrections, which were implemented in a slightly different way in the two data processing software packages. Furthermore, it was shown that incorrect H_2O corrections may yield false diel

patterns to CH_4 fluxes. These results exemplify the fact that EC data processing may generate apparent differences between CH_4 fluxes, which hinder the cross-comparison of CH_4 fluxes measured at different sites. Thus scientists are encouraged to perform flux data processing program comparisons periodically, so that biases between software packages can be monitored and possibly minimized. Also, regular usage of several different software packages (e.g. EddyUH, EddyPro or similar) to process the same EC data may be advantageous, since it decreases the possibility of erroneous data processing.

3) *to determine the spatial representativeness of short tower EC CH_4 fluxes in an agricultural peatland landscape*
Three short EC towers separated 2–3 km from each other were used to estimate the spatial variability of ecosystem scale ($\sim$ 1 ha) EC CH_4 fluxes. The CH_4 flux spatial variability was of similar magnitude as the temporal variability, unlike for the other fluxes (sensible heat flux and friction velocity) measured at the three sites for which the spatial variability was an order of magnitude smaller than the temporal variability. For long-term cumulative emissions, the CH_4 flux spatial variability was 14 % of the mean cumulative emission and it was shown to contribute up to 50 % of the uncertainty of annual CH_4 emissions.

4) *to evaluate the applicability of a tall flux tower EC system in measuring landscape scale CH_4 emissions*
CH_4 fluxes were measured at a tall flux tower in order to evaluate whether such a measurement system could be used to estimate landscape scale CH_4 emissions directly. It was shown that the transition periods between stably stratified night time and unstable daytime were problematic for the tall flux tower measurements and spurious differences between the short tower and tall tower CH_4 fluxes were observed during these periods. It should be noted however, that these periods are often tricky also for short towers. Furthermore, the large footprint of the tall flux tower system contained emissions from several sources with different emissions strengths and patterns and their separation from each other required elaborated data analysis. Despite these shortcomings, tall tower EC system was concluded to be a viable way to estimate landscape scale fluxes.

A few general concluding remarks can be drawn from the results presented in this thesis. The high precision of modern EC CH_4 analysers allows EC studies to be conducted in locations which were previously 'out of reach'. Exchange at ecosystems with low CH_4 emissions (e.g. lakes, rivers or wet upland forests) can be measured with the modern instrumentation. This opens yet largely unexplored area to be studied and the increase of EC CH_4 studies shown in Fig. 1 can be projected to continue. However, as the signal (i.e. CH_4 flux) is weak in these ecosystems, special care should be taken when processing the data, since significant systematic uncertainties may originate from poorly executed processing. Fortunately, the EC data processing and instrumentation will be standardised within the international measurement networks being initiated (e.g. ICOS, NEON) which will limit the possibility of erroneous corrections and improve the cross-comparison of EC CH_4 fluxes from different sites. The work conducted in this thesis is currently utilised in this standardisation process.

The systematic uncertainties outlined above indicate that the CH_4 flux spatial variability is the main reason why large scale CH_4 budgets cannot be readily obtained from short tower EC measurements. Thus in order to estimate accurate landscape scale CH_4 budgets, efforts should be put on understanding the flux spatial variability, from plot to ecosystem and finally to whole landscape level emissions. Hopefully the future work on this issue will benefit from the results presented in this thesis.

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